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Paleoenvironments and Hydrocarbon Potential of Upper Cretaceous Shales in Agbabu-1 Well, Dahomey Basin SW Nigeria

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Abstract

Upper Cretaceous shales partially exposed in the northern fringes of the Dahomey Basin are well developed in the subsurface in Southwestern part of the basin where Agbau-1 well is sited. These shales were evaluated in respect to their paleoenvironments and potentials for hydrocarbon using foraminiferal assemblages, biomarkers and Rock Eval pyrolysis studies. The dominance of benthonic foraminifera species suggests a shallow marine environment and high percentage of calcareous to arenaceous benthic foraminifera indicate high water salinity and hypersline environment. Dysoxic oxygen condition is also prevalent probably because most of the benthic foraminifera recovered are epifauna that live in a reduced oxygen condition. 1.90 wt%, 244 mgHC/gTOC and 429℃ average values of total organic carbon, hydrogen index and Tmax reveal that the Upper Cretaceous shales have relatively fair to good organic matter, predominantly Type II-III kerogen and currently immature. Though three is a trend of an increase in maturity down the hole. All the steranes have uniform distributions (C27>C28>C29), suggesting a relatively higher input from the marine red algae and a low level of land plant contribution to the source organic matter. Pristane/phytane ratios and C29/C27 steranes confirmed the organic matter type to be a Type II/III and anoxic source rock depositional condition as well as a reducing diagenetic system in the sediment water column. The Upper Cretaceous shales in Dahomey Basin can be targeted for exploration as an unconventional petroleum resource.

1.0 Introduction

Hydrocarbon production from the prolific Niger Delta basin has been the most valuable source of income and energy in Nigeria. However, hydrocarbon resources are being depleted daily and the need to explore more hydrocarbon plays have never been more important. Rigorous exploration activities in the adjacent frontier basins and deeper Cretaceous plays are among the few options of supplementing the depleting Niger Delta resources. The discovery of oil in offshore Cretaceous sediments of the Ise Formation in the Gulf of Guinea has increased the study and search for oil in the eastern Dahomey Basin. The source rock within this formation has a Type I kerogen with a Total Organic content of 4% and hydrogen index (HI) greater than 500 g/gram (Brownfield and Charpentier, 2006). Lower Cretaceous lacustrine source rocks with kerogen within the oil windows were identified in the far west of Ivory Coast basin (Elvsborg and Dalode, 1985; Abacan-Addax Consortium, 1998). Further studies on two Cenomanian shales samples in the underlying Abeokuta Formation (presents day Afowo formation) by (Beicip-Franlab, 1994 and Adeoye et al., 2020) showed a TOC range of 4.2 and 7.1 wt.% with HI values of 324 and 531 mg HC/gTOC as potential resources for more discovery of oil and gas to increase the national reserve.

The eastern section of the Dahomey basin also contains more hydrocarbon resources in term of extensive tar sand deposits within the Abeokuta Group (Ise, Afowo and Araromi Formations), which extends over a belt of 120 km long (Enu, 1987). Ekweozor and Nwachukwu (1989) and Ekweozor and Telnaes (1990) examined the origin and composition of the tar sand from the Abeokuta Group.

Adekeye and Akande, (2010) had contributed information on some geochemical properties of Upper Cretaceous sequences from the Gbekebo and Araromi borehole. This present study aims to evaluate the paleoenvironments and hydrocarbon potential of the Upper Cretaceous shales in Agbabu-1 well through foraminiferal paleontological, Rock Eval pyrolysis, and biomarker characterization to assess their possible contribution to the petroleum resources of the basin be it conventional or unconventional.

2.0 Geologic Setting

Dahomey Basin is part of the West African margin sag basin system (Klemme 1975; Kingston et al., 1983). The rifting and opening up of Gulf of Guinea through the separation of the African and South American plate is connected to the evolution of the basin (Storey, 1995; Mpanda, 1997). It is a coastal sedimentary basin that is adjacent to the present-day Gulf of Guinea and extends from southeastern Ghana, along Togo, Benin and Southwestern Nigeria (Burke et. al., 1971). The boundaries are defined on the western flank by the Ghana ridge and extensions of the Romanche fracture zones, on the eastern flank they are bounded by the Benin hinge line. The hinge line separates the Okitipupa ridge from the adjacent Tertiary Niger Delta (Adegoke 1977, Elvsborg and Dalode, 1985; Omatsola and Adegoke, 1981). Massive deposition of thick non-marine sediments accompanied the late Jurassic and early Cretaceous rifting and graben formation and these sediments in combination with the basement floor, block faulted and further created a series of horst and graben (Omatsola and Adegoke, 1981). Hessouh et al., (1994) worked on seismic data and subsurface structural models to understand the tectonics and sedimentary history of some parts of the Dahomey basin. They divided the tecno-sedimentary into four (4) stages from the oldest to youngest as: pre-rift (up to late Jurassic), syn-rift (Neocomian to lower Cretaceous), transitional (Cenomanian to Santonian) and post-rift (Maastrichtian to Holocene). (Adegoke, 1969; Ogbe, 1970; Kogbe, 1974; Billman, 1976; Omatsola and Adegoke, 1981; Ako et al., 1980; Okosun, 1990; Idowu et al., 1993; Adekeye, 2005 and Adekeye et al., 2006) have studied the stratigraphic framework, sedimentology and depositional settings of the Dahomey basin (Fig. 1). They identified five formations within the Cretaceous and Tertiary ages. The formations from the base to top include: Abeokuta Group comprises of Ise, Afowo and Araromi Formations (Cretaceous), Ewekoro Formation (Paleocene), Oshosun Formation (Eocene) and Ilaro Formation (Eocene) (Fig. 2). This work examines the Araromi Formation, which is mainly a shale lithology with thin intercalations of marl and limestone (Omatsola and Adegoke, 1981). The shale is grey to black and has a high organic content with beds of lignite at the shallow depth. The formation is similar in composition to the Nkporo shale and does not outcrop anywhere within the basin (Okosun 1990). (Jan du Chene, 1977, Adegoke et al., 1980) assigned a Maastrichtian to Paleocene age to the Araromi Formation with respect to its fossil contents.

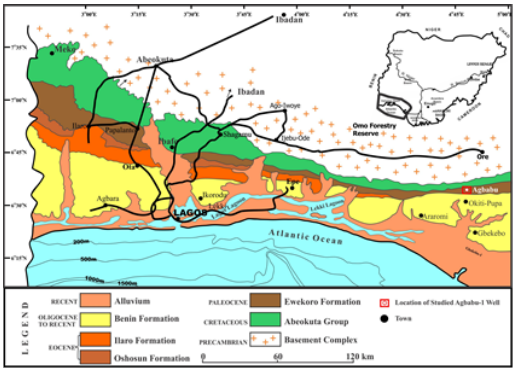


Fig. 1. The outline geological map of Dahomey Basin (Modified after Adekeye et al., 2019)

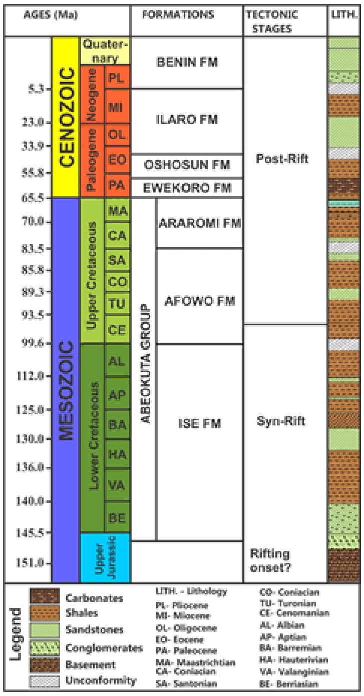


Fig. 2. Chronostratigraphic chart of the Dahomey Basin showing key tectonic stages in relation to the geologic formations and lithologies (Modified from Adeoye et al., 2020)

3.0 Methodology

3.1. Rock Eval Pyrolysis

Twenty (20) drill cuttings samples were collected within the interval 1128 m to 2181 m from the Agb_1 well in the eastern part of Dahomey basin in Southwestern Nigeria. The samples were crushed and pulverized into a 250 microns mesh (US mesh 60) in preparation for the analysis. About 60 – 80 mg of the pulverized samples were transferred into the crucibles in the UND-Weatherford Source Rock Analyzer. The first crucible in the sequence is blank, this is done to allow the machine perform a blank correction for all the subsequent samples in the crucibles. The analysis involves loading of a standard sample after every five (5) samples, to ensure quality assurance and quality of results. Operating procedures for programmed Rock-Eval pyrolysis involves heating 60-80 mg of pulverized samples at 300°C for 3 minutes, followed by programmed pyrolysis at 25°C/min to 650°C in a helium atmosphere (Clementz et. al., 1979). Hydrocarbons liberated from the samples during pyrolysis are detected by a flame ionization detector (FID) within the equipment. The various measurements determined from rock eval pyrolysis includes S_1, S_2, S_3, TOC, Tmax, OI, HI, PI

3.2 Extraction and Fractionation

Samples from the Araromi well were crushed and pulverized in a rotary mill. The powdered samples were then soxhlet extracted in pre-extracted cellulose thimble with azeotropic mixture of redistilled dichloromethane/methanol (93:7, v/v) for 24hours. Copper turnings were added to remove the elemental sulphur in the samples. An aliquot of the total extractable organic matter (EOM) for each sample was fractionated into aliphatic and aromatic hydrocarbons, and NSO/resin fractions by thin layer chromatography (TLC, Kieselgel 60G,) using petroleum ether as the developer. The separated aliphatic and aromatic hydrocarbon fractions were submitted for GC and GC-MS analyses.

3.3 Gas chromatography (GC)

GC was carried out on the aliphatic hydrocarbon fractions for their *n*-alkane distribution using an HP 5890 series II GC fitted with HP-5 fused silica capillary column (30m x 0.25mm i.d., 0.25µm film thickness). The oven was programmed to run at 50^{o}C (2 min) and the temperature was ramped from 50^{o}C to 300^{o}C at 4^{o}C /min, followed by a 20 min isothermal condition at 300^{o}C. Hydrogen was used as the carrier gas at a flow of 2 mL/min.

3.4 Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS analysis of aliphatic and aromatic fractions was performed on a Hewlett Packard 6890 GC split/splitless injector (280°C) linked to a Hewlett-packhard 5973 mass selective detector (electron voltage 70eV, filament current 220ɥA, source temperature 230^{0}C, quad temperature 150°C, multiplier voltage 2500V, interface temperature 310°C). The acquisition was controlled by a HP Kayak chemstation computer, initially in full scan mode (TIC; 50-550 amu/sec) or in selected ion mode (SIM; 30 ions 0.7cps 35ms dwell) for greater sensitivity. The sample (1ul) in methylene chloride was injected by an HP7683 auto sampler and the split opened after 1 minute. After solvent peak had passed the GC, temperature programme and data acquisition commenced. Compounds separation was performed on a fused silica capillary column (60m x 0.25mm i.d.) coated with 0.25µm 5% phenyl dimethyl Polysiloxane (HP-5). The GC was temperature programmed from 40°C to 300°C at 4°C /min and held at 300°C for 20 min with Helium as the carrier gas (flow 1mL/min, initial pressure of 50kPa, split at 30 mL/min).

3.5 Gas Chromatography Mass Spectrometry/ Mass Spectrometry (GC-MS/MS)

GC-MS/MS was performed on the aliphatic fractions of sample Ar-145 using a Varian 1200 quadrupole MS/MS fitted with an HP-5 MS (5% phenyl di methyl polysiloxane) fused silica capillary column (30m x 0.25mm i.d. x 0.25µm film thickness. The GC separated components were transferred via the heated transfer line to the ion source. Electron impact mode was used for ionisation at 70eV. The oven temperature programme was 40°C (0 min), ramped from 40°C to 175°C at 10°C /min (held for 1 min at 175^{0}C), 175°C to 225°C at 6°C/min (with a hold of 1 min. at 225°C) and then ramped to 300°C at 4°C /min with an isothermal condition of 20 min at 300°C.

3.6 Foraminiferal Palaeontology

The Twenty (20) cuttings from Agbabu-1 well were digested in the laboratory using hydrogen peroxide (H_2O_2) and water H_2O in the ratio of 3:1. The solution was transferred into each of the samples in labelled containers and soaked for twenty-four hours to ensure proper digestion. The digested samples were washed through a 0.63-micron sieve under a jet of running water until all the clay particles are completely removed. The samples were carefully transferred back into the containers, filled with water, allowed to settle before decanting. The samples were dried on a hot plate and transferred into labelled envelops. A Reflected Light Microscope (RLM) was used in picking the microfossils from the washed residues. This is done by spreading a small quantity of the dried sample evenly on a picking tray. The foraminifera content was carefully picked with the aid of a picking brush and transferred into the cellules. The cellules were labelled according to their depths and covered with cover slips to prevent the loss of the specimen.

4.0. Results And Discussions

4.1paleoenvironments

4.1.1Foraminiferal Assemblages

The distribution of foraminifera may vary according to various combined factors such as substrate type, light intensity, water temperature, food availability oxygen, salinity and current energy according to Murray and Wright (1974). Many of these factors vary with water depth, so depth may capture variations in these parameters and in species distributions. Few planktonic and reasonable number of benthic number of foraminifera were identified and picked from the samples. The planktonic foraminifera species which were identified include; *Globotruncanella petaloidea, Globotruncana gansseri, Globotruncana navaroensis,Gobotruncana aegytiaca, Heterohelix globulosa and Abathomaphalus mayaroensis.* The Benthic foraminifera species which were identified include; *Afrobolivina afra, Nonionella auris., bolivina Africana, Ninion sp., Bolivina explicate, Valvulineria sp.,Texrtularia h^{oc}kleyensis, Cyclammina cancellata, Haplophragmoides sp., and Ammobaculites sp.* Fig. 3 showed some of the planktonic and benthonic foraminifera species identified. Results from individual foraminifera counts are eight (8) planktic, thirty-one (31) calcareous and eighteen (18) Arenaceous (Fig. 4). These results showed that the calcareous foraminifera species were abundant and diverse at the deeper part of the well while the arenaceous foraminifera species dominates the shallow portion of the well (Fig. 4). The total distribution for the planktonics, calcareous and arenaceous foraminifera counts is 14%, 54% and 32% respectively.

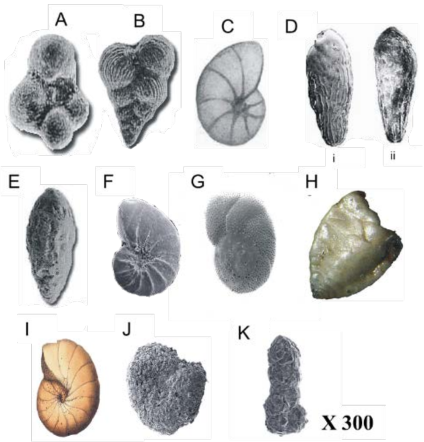


Fig. 3. Photomicrograph of some of the foraminifera identified. (A) *Globotruncanella petaloidea* (B*) Heterohelix globulosa* (C) *Nonionella auris* (D) {i} *Afrobolivina afra {ii} Bolivina Africana* (E) *Bolivina explicata (*F) *Nonion sp* (G) *Valvulineria sp* (H) *Textularia hockleyensis* (I) *Cyclammina cancellata* (J) *Haplophragmoides sp* (K) *Ammobaculites sp*

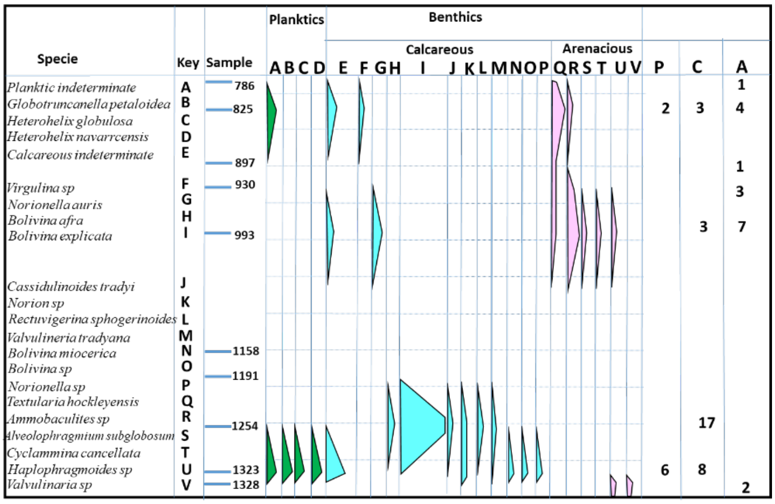


Fig. 4. Recovered planktonics and benthonics foraminifera and count/depth of species in the Agbabu-1 Well

4.1.2 Benthic Foraminifera and Paleoecology

The paleoecology interpretation of ancient sediments has been made possible with the aid of benthic foraminifera occurrence, which indicate a wide range of possible water depth which the fossil could withstand (Gebhardt, 2004). This is carried out by correlating modern ecological settings and their fauna, although it is believed that some taxa have changed their environmental preference through time. Species diversity is another general indicator of how conducive the environment may be from some foraminifera taxa to populate. Low number of species suggest environmental stresses while high diversity suggests favourable conditions (Murray and Wright, 194). The occurrence of diagnostic benthic species all the definition of minimum and maximum water depth for different part of the well section. High diversity of arenaceous foraminifera indicate low-oxygen concentrations (Gebhardt, 1998). This could be a result of increased input of organic matter from incoming fluvial systems. The shell type such as; Agglutinated, Porcelaneous calcareous and Hyaline calcareous ratio is used in salinity interpretation (Murray and Wright, 1974). The ratio of these test types has been used in differentiating brackish from hypersaline and normal marine environments.

In reconstructing bottom water oxygenation benthic foraminifera assemblages are used. Deep ocean oxygen concentration has a profound impact on marine benthic foraminifera distribution pattern in modern and ancient oceans. As global temperature rise, areas of oxygen-poor environments, which include Oxygen Minimum Zones (OMZs), are predicted to increase, and with this, foraminifera show preference to varying oxygen condition. Many researchers that use foraminifera to evaluate bottom water oxygen (BWO) concentrations consider epifaunal species as indicators of well-oxygenated environments (Kaiho, 1999). The benthic foraminifera are grouped into oxygen indicator categories that is; oxic, suboxic and dysoxic. Deep infauna taxa dominate organic-rich, oxygen depleted environment is regarded as indicators for oxygen depleted environment (Bernhard, 1986). Based on these paleoecologic interpretations of different authors, sediments in this present work are suggested to be deposited in a shallow marine environment due to the dominance of benthonic foraminifera species. Also, the percentage of calcareous to arenaceous benthic foraminifera in the well (Fig. 4) is relatively high and this is an indication of high water salinity and hypersaline environment. The oxygen condition suggests a dysoxic condition because most of the benthic foraminifera recovered are epifauna that live in a reduced oxygen condition.

4.1.3 Depositional Condition

Pristane and phytane are isoprenoids that are commonly used to infer depositional conditions for organic rich sedimentary rocks as well as oils derived from those rocks because of the difference in their diagenetic fate under anoxic and oxic conditions. Phytane formation from the phytol side chain of chlorophyll-a is favoured under a reducing condition (low Eh) while oxic condition (high Eh) favours formation of pristane from the same phytol precursor. In keeping to this theory, the depositional conditions for these samples have been inferred from the pristane and phytane ratios. Most of the samples generally have pristane/phytane ratio between 0.8 – 1.2 (Table 2) suggesting that the organic matter type is likely to be a Type II/III or II-S and anoxic source rock depositional condition as well as a reducing diagenetic system in the sediment water column (Didyk et. al., 1978; Volkman and Maxwell 1986). A plot of these pristane/phytane ratios against C_{29}/C_{27} steranes permits a visual assessment of the organic matter type as well as the depositional condition (Fig. 5) for the Araromi shale samples assessed in this work.

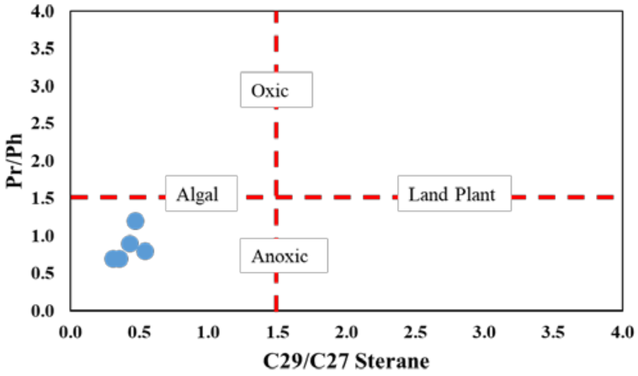


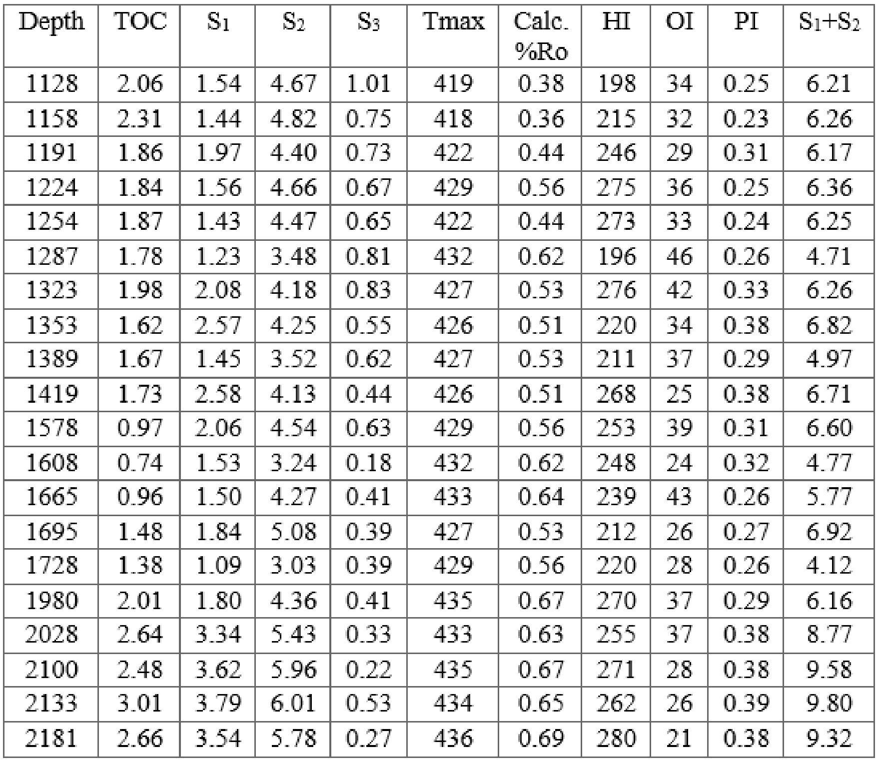
Fig. 5. Plot of Pr/Ph against the C_{29}/C_{27} sterane used as an estimate of the redox state and predominant organic matter type from the isoprenoids and steranes. All the samples plot in the anoxic and algal dominated zone. Note boundaries are not definitive

It is noteworthy to add that the copper turnings that were recovered from the EOM after the 24-hour period of extraction turned black completely for most of these samples This is an indication of the high sulphur content present in these samples. Although sulphur content was not measured directly, this is an '*informed*' measurement of sulphur level as either low or high in a source rock extract. Sulphur incorporation into organic matter occurs during diagenesis by a microbially –mediated (*desulfovibrio bacteria)* sulphate reduction process under a low Eh condition (Peters et. al., 2005). Further, this observation of high sulphur in addition to the calculated pristane and phytane ratios supports a highly reducing depositional condition for these samples. The low thermal level of maturation for the sample set do not permit the measurement of the homohopane index which may further lend weight to the inferred redox condition from the isoprenoid ratios.

4.2 Hydrocarbon Potential

Rock Eval Pyrolysis and biomarker data from the shales from Agbabu-1 well were evaluated to determine the quantity, types, depositional condition and thermal maturity of organic matter in the Upper Cretaceous sequence as presented in Table 1 and Table 2.

Table 1. Rock–Eval pyrolysis data for the Araromi Formation source rocks in Agbabu-1 Well



Depth	TOC	S_1	S_2	S_3	Tmax	Calc. %Ro	HI	OI	PI	S_1+S_2
1128	2.06	1.54	4.67	1.01	419	0.38	198	34	0.25	6.21
1158	2.31	1.44	4.82	0.75	418	0.36	215	32	0.23	6.26
1191	1.86	1.97	4.40	0.73	422	0.44	246	29	0.31	6.17
1224	1.84	1.56	4.66	0.67	429	0.56	275	36	0.25	6.36
1254	1.87	1.43	4.47	0.65	422	0.44	273	33	0.24	6.25
1287	1.78	1.23	3.48	0.81	432	0.62	196	46	0.26	4.71
1323	1.98	2.08	4.18	0.83	427	0.53	276	42	0.33	6.26
1353	1.62	2.57	4.25	0.55	426	0.51	220	34	0.38	6.82
1389	1.67	1.45	3.52	0.62	427	0.53	211	37	0.29	4.97
1419	1.73	2.58	4.13	0.44	426	0.51	268	25	0.38	6.71
1578	0.97	2.06	4.54	0.63	429	0.56	253	39	0.31	6.60
1608	0.74	1.53	3.24	0.18	432	0.62	248	24	0.32	4.77
1665	0.96	1.50	4.27	0.41	433	0.64	239	43	0.26	5.77
1695	1.48	1.84	5.08	0.39	427	0.53	212	26	0.27	6.92
1728	1.38	1.09	3.03	0.39	429	0.56	220	28	0.26	4.12
1980	2.01	1.80	4.36	0.41	435	0.67	270	37	0.29	6.16
2028	2.64	3.34	5.43	0.33	433	0.63	255	37	0.38	8.77
2100	2.48	3.62	5.96	0.22	435	0.67	271	28	0.38	9.58
2133	3.01	3.79	6.01	0.53	434	0.65	262	26	0.39	9.80
2181	2.66	3.54	5.78	0.27	436	0.69	280	21	0.38	9.32

Table 2. Results of n-alkanes, isoprenoids, terpanes and steranes molecular parameters measured for the samples

Sample I. D	Pr/ Ph	Pr/ nC_{17}	Ph/ nC_{18}	CPI	Ts/ Ts+Tm	C31 αβ Hopane	C29ααα Sterane	% C27	% C28	% C29	% C30
Ar-88	0.8	0.5	0.2	1.1	n.m	n.m	0.09	54	17	29	n.m
Ar-145	0.9	1.1	0.8	0.9	0.18	0.18	0.05	49	30	21	6.0
Ar-148	0.7	0.6	0.7	2.3	0.15	0.15	0.13	59	23	18	n.m
Ar-149	1.2	1.2	0.7	1.5	0.19	0.18	0.11	51	25	24	3.6
Ar-151	0.7	0.5	0.5	0.9	0.43	0.46	0.22	54	27	19	2.7

4.2.1 Quantity of Organic Matter

The data showed that TOC range from 0.74 wt.% to 3.01 wt.% with an average of 1.85 wt.% within the Araromi Formation. Also, the S_2 value range from 3.03 to 6.01 mg HC/ g rock with average of 4.51 mg HC/ g rock. The

TOC is the mass of carbon per unit mass of the whole rock determined by summing the carbon in the pyrolyzate (S_1, S_2 and S_3) with the carbon obtained by oxidizing the residual organic matter after heating to 650 °C (Peters, 1986). The S_2 is the amount of hydrocarbon (mg HC/g rock) liberated by thermal degradation of the kerogen in the rock at temperature between 300-550°C. This work utilized Peter and Cassa (1994) classification of organic richness in source rock with respect to TOC and S_2 values (Fig. 6). The data points range from fair to very good zone of source rock quantity. The TOC in the lower part of the Araromi formation are relatively higher than the TOC from middle and upper part. An explanation to this is that the base of Araromi formation uncomformably overlain the deep-seated bitumen rich Turonian – Coniacian sediment, which is believed to be a contributing factor to its relatively higher TOC.

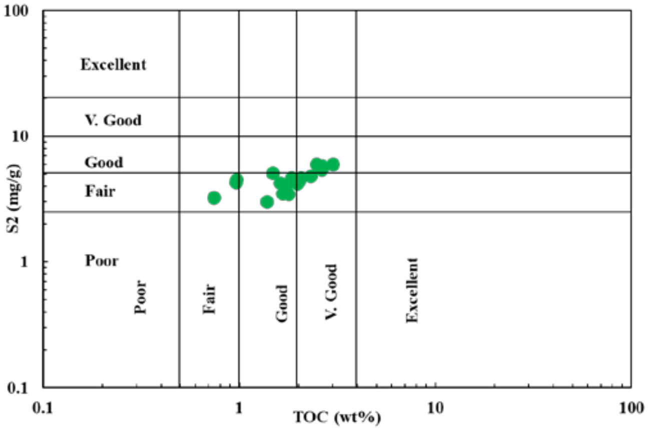


Fig. 6. Quantity and quality of organic matter in the studied wells from TOC and S2 analysis

4.2.2 Types of Organic Matter

The precursor(s) (type) of organic matter preserved in these shale samples as well as the depositional conditions (redox potential) were examined through the integration of a battery of molecular geochemical parameters ranging from pyrolysis biomarker data.

The hydrogen index (HI) values range from 196 to 280 mg HC/gTOC with an average of 244 mg HC/gTOC and the oxygen index range from 21 to 46 mg CO_2/gTOC with an average of 33 mg CO_2/gTOC. The nature of organic matter making up the source rock is a useful tool in determining the oil and gas potential of the source rock. Espitalie et al., 1977 classified kerogen types using pyrolysis data because they were not controlled by organic matter abundance, instead, they are influenced by the elemental composition of kerogen. They classified kerogen types with a modified Van Krevelen diagram by substituting H/C with HI and O/C with OI data from the pyrolysis. On the modified diagram, Type I kerogens are characterized with relatively high HI and low OI, Type III kerogens have relatively low HI and high OI, and Type II kerogen are intermediate. In the plot of HI vs. OI (Fig. 7), all the data points fall within the lower limits of the Type II zone. In addition, the Langford and Blanc-Valleron (1990) plot was also used to determine the genetic type of organic matter. Based on this TOC vs S_2 cross plot (Fig. 8), all the data points are within the type II-III zone except for two data points in the type II zone. The results showed that Araromi source rock are dominated by marine algae materials with some terrestrial influence. The HI range of 196 to 280 mgHC/gTOC also falls within the Waples (1985) Type II classification.

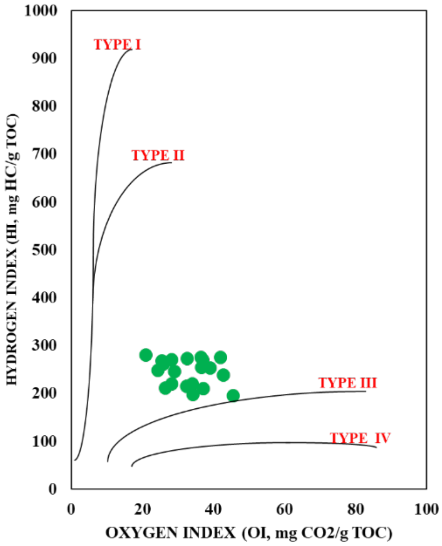


Fig. 7. Organic matter types within Araromi Formation source rock as indicated from OI and HI

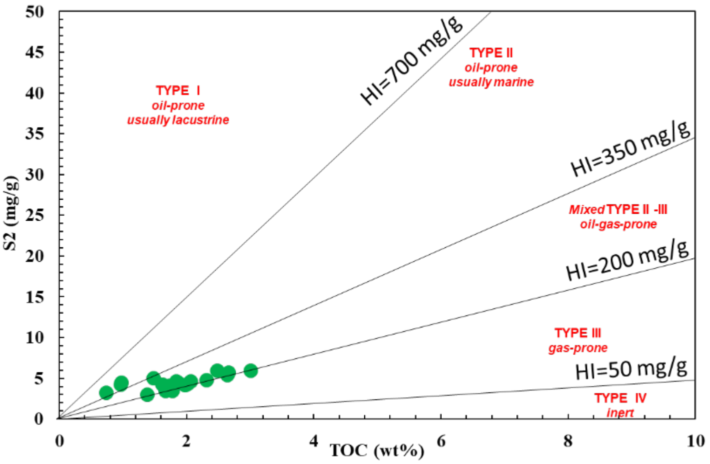


Fig.8. Cross plot of S_2 and Toc for determining kerogen types

n- Alkanes Distribution

Bray and Evans (1961) have shown that the normal alkane (*n*-alkane) chain length is a function of the type of fatty acid synthesized biologically. Marine algae make shorter *n*- alkane chains than terrigenous higher plants. Because of this, most algae and bacterial derived *n*-alkane usually show a maximum between nC_{17} and nC_{21}, while terrigenous higher plants typically produce *n*-alkanes that maximizes around nC_{29}. Most of the samples analysed by GC display a bi-modal *n*-alkane envelope with maxima between nC_{16} and nC_{18}, and nC_{27} and nC_{29} respectively (Fig. 9), suggesting that the source organic matter have been derived from a variable mixture of algae and terrigenous higher plants materials. However, sample Ar-145 (Fig. 10) display an almost unimodal *n*-alkane profile typical of a dominantly normal marine algal contribution (i.e. maximizing between nC_{16}- nC_{18}) (Jacobson et. al., 1998).

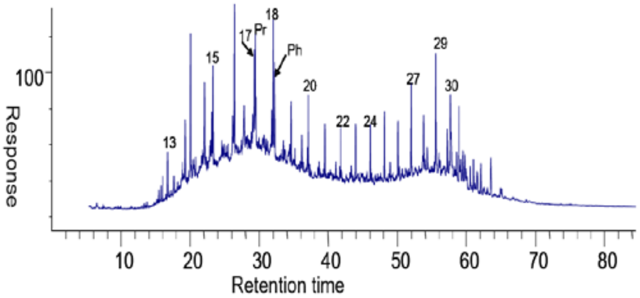


Fig. 9. A bimodal *n*- alkane envelope of sample Ar-149 maximizing at nC_{16} and nC_{29} typical of source rock whose organic matter have been derived from a variable mixture of algal and

terrigenous higher plant materials. Note 13, 15, etc. represents the *n*-alkane carbon numbers and Pr; pristane, Ph; phytane

Fi

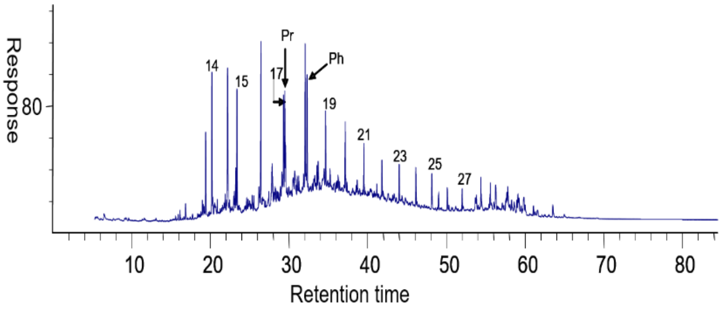


Fig. 10. A unimodal *n*- alkane envelope of sample Ar-145 maximizing at nC_{16} typical of a dominantly marine algae contribution to the organic matter. Note 14,15, etc. represents the *n*-alkane carbon numbers

The calculated carbon preference index which measures the proportion of the odd to even-carbon numbered *n*-alkane (CPI_1 in the range nC_{24} – nC_{34}; Bray & Evans, 1961) ranges in value from 0.9 - 1.1 for most samples except for sample Ar-148 and Ar-149. This general CPI range is indicative of a dominantly marine algae contribution to the source organic matter for these samples (Scalan & Smith, 1970). This inference of a significant marine algal derived organic matter is further strengthened by the sterane carbon distribution as discussed in the later sub-section.

Sterane Carbon Distribution

On the basis of differences in the source of cholestane (C_{27} sterane derived mainly from marine red algae), ergostane (C_{28} sterane derived predominantly from algae of marine and or lacustrine ecology) and stigmastane (C_{29} sterane derived predominantly from higher plants and a few non-marine green and brown algae), the relative abundances of these sterane compounds in sediment EOM and crude oil have always been used as a proxy for level of contribution of their precursors to the source organic matter (Moldowan et. al., 1985). From the sterane carbon distribution as shown in the ternary plot (Fig. 11), most samples contain dominantly of the C_{27} sterane and less than 30 % of C_{29} sterane , suggesting a relatively higher input from the marine red algae and a low level of land plant contribution to the source organic matter (Goodwin, 1973). All the steranes have similar distributions in the studied wells (C27>C28>C29) as seen in Table 2.

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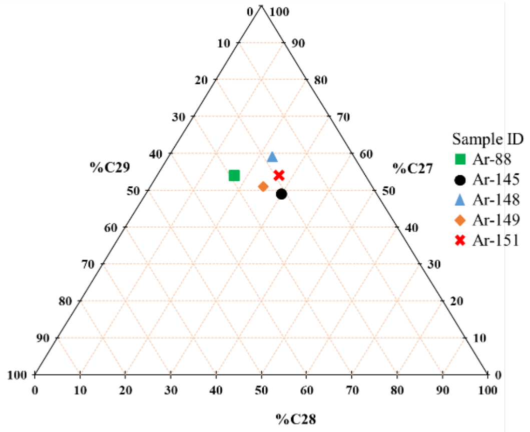

Fig. 11. A triplot of the sterane carbon number distribution using the % C_{27}, % C_{28} and the % C_{29} ααα R steranes from m/z 217 mass chromatogram. Data plot show that all of the samples contain less than 30 % of C_{29} sterane; this suggests a low level of land plant contribution to the source organic matter

C_{30} Sterane

Sterane containing 30 carbon atoms i.e. 24-*n*-propylcholestane has been shown to be derived predominantly from the C_{30} sterol of the lipid membrane of marine *chrysophyte* algae (Rohmer *et. al*., 1980). By extension of this reasoning, the occurrence of C_{30} sterane in the Araromi samples (Fig. 11) has been investigated and representative samples contain measurable amount (Table 2). This suggests a marine origin for the source rock kerogen.

Triterpanes

Although the samples are immature, their triterpane distributions offer an excellent opportunity to corroborate the previous assertion that there is generally a very low level of land plant contribution (app. 30% C_{29} sterane in all) to the sedimentary organic matter for all of these samples. The absence of oleanane (a biomarker highly diagnostic of angiosperm land plant) in all of the samples suggests a restricted land plant contribution (Ekweozor and Udo, 1988). Although abundant oleanane occurrence has also been shown to be restricted to sediments not older to Late Cretaceous (Moldowan *et. al*., 1994). This observation of an absence of an oleanane peak in the m/z 191 of all of the samples analysed in this Araromi shale samples set is consistent with the findings of Ekweozor and Udo (1988) who first reported the paucity of oleanane in Abeokuta Group shale samples. The absence of oleanane has been attributed probably to the separation of the Anambra and Dahomey epeiric seas by Okitipupa ridge during the Upper Cretaceous thus giving rise to the restriction of oleananes (angiosperm precursors) to the south-eastern Nigerian sedimentary basins and their absence in the south-western Dahomey Basin (Ekweozor and Udo, 1988).

4.2.3 Thermal Maturity of Organic Matter

Tmax

The thermal maturity is determined from Tmax, the temperature at which the S_2 peak is maximum. The value ranges from 418°C to 436°C with an average of 429°C in the Araromi well. Thermal maturity describes the overall temperature influence that converts organic matter in sedimentary rocks to petroleum products. They are classified into immature, mature and post mature with regards to temperature (Peter and Cassa, 1994). The nature of organic matter and extent of thermal maturity controls type and distribution of petroleum products within a given source rock (Tissot and Welte 1984, Langford and Blanc-Valleron 1990). Tmax is influenced by the type of organic matter and show relatively higher values in marine and lacustrine organic matter (Tissot and Welte 1984). Peter and Cassa 1994, Hunt (1996) identified the various Tmax ranges for different stages of maturity in a source rock. They are <435°C for immature rocks, 435°C – 470°C for the mature zones and >470 °Cfor post mature. The Tmax values in this well are all below the 435°C maturity cut-off except for three data points in the lower part of the well (Fig. 12).

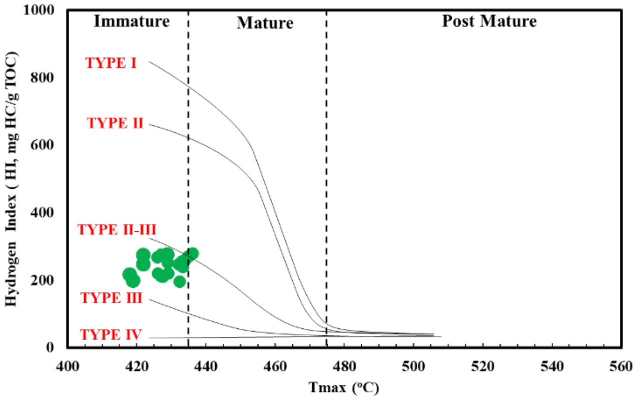

Fig. 12. Thermal maturation and types of organic matter from Tmax and HI

Further maturation indices of Hopanes and steranes isomerisation maturity parameters were calculated from integrated peak heights in the m/z 191 for hopanes and m/z 217 mass chromatogram for sterane. Values for the measured thermal maturity parameters are presented in Table 2. The samples are generally immature (very low values generally less than 0.25) except for sample Ar-151 which is mature for the measured parameters. In general, there is a good agreement among the calculated Ts/Tm, C_{31} αβ Hopane and the ααα C_{29} sterane maturity parameters for the samples. αββ C_{29} sterane maturity parameter could not be calculated because of their low concentration at this thermal level for the samples. Fig. 13 is an m/z 191 mass chromatogram showing a representative distribution of the terpenoids in sample Ar-I45.

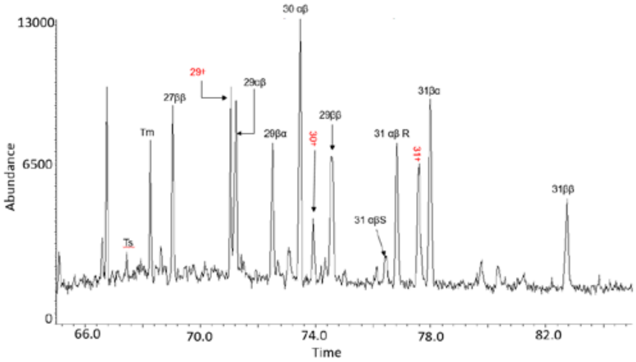

Fig. 13. m/z 191 mass chromatogram of sample Ar-145 showing the terpenoids distribution. Numbers refer to carbon numbers. ββ, βα, αβ, refer to the stereochemistry at the 14 and 21 carbon number respectively in the hopanes structure. Labels in red (e.g. 29†) are Hopenes. Ts and Tm refer to 17α (H), 22, 29, 30-trisnorhopane and 18α (H), 22, 29, 30-trisnorneohopane respectively. Compounds have been identified by TIC GC- MS and by GC-MS/MS parent to daughter ion transition

6.0. Conclusions

The following conclusions can be drawn from this study:

- The Araromi Shale in the study area are dominated by organic matter that are < 3 wt.% TOC, with the highest values from samples at the base of the formation.
- The source rock is made up of Type II kerogen, further classification scheme showed they are mainly Type II-III
- The samples from AGB-1 well are generally immature, only samples that are believed to be influenced by the underlying bitumen reached the 435°C-maturity cutoff. Also, Hopanes and steranes isomerisation maturity parameters in studied samples showed the that the Araromi shale is immature except for sample Ar-151
- *n*- Alkanes distribution showed bimodal signature between nC_{16} - nC_{18} and nC_{27} - nC_{29} with a unimodal nC_{16} - nC_{18} signature suggesting variable mixture of marine algae and terrigenous higher plants materials. The inference of a significant marine algal derived organic matter is further strengthened by the C27>C28>C29 sterane carbon distribution

- Triterpanes studies showed that the absence of oleanane (a biomarker highly diagnostic of angiosperm land plant) in all of the samples suggests a restricted land plant contribution
- Pristane/phytane ratio suggested that the organic matter type is dominantly Type II/III with an anoxic source rock depositional condition as well as a reducing diagenetic system in the sediment water column. The reducing diagenetic system is also supported with the presence of high Sulphur content.
- Biostratigraphy data suggested a shallow marine environment due to the dominance of benthonic foraminifera species. Also, the percentage of calcareous to arenaceous benthic foraminifera in the well is relatively high and this is an indication high water salinity and hypersaline environment. The oxygen condition suggests a dysoxic condition because most of the benthic foraminifera recovered are epifauna that live in a reduced oxygen condition
- The overall assessment reveals that the Upper Cretaceous shale in this study and other previous work is some potential resources for unconventional hydrocarbon exploration

Appendix

TOC - Total Organic Carbon, wt. %
S_1 - volatile hydrocarbon (HC) content, mgHC/grock
S_2 - remaining HC generative potential, mgHC/grock
S_3 - carbon dioxide content, mg CO_2 /g rock
Tmax°C - Maximum S_2 Temperature
Ro - Vitrinite reflectance
HI - Hydrogen index = S_2 x 100 / TOC, mgHC/gTOC
OI - Oxygen Index = S_3 x 100 / TOC, mgCO_2/gTOC
PI - Production Index = S_1 / (S_1+S_2)
S_1+S_2 Generating Potential (HC) content, mg HC/grock
Pr/Ph: ratio of Pristane to Phytane calculated as the ratio of their peak heights from the GC mass chromatogram;
Pr/nC_{17}, Ph/nC_{18}: ratio of peak heights of pristane/nC_{17} and phytane /nC_{18} from the GC mass chromatogram;
Ts/ Ts+Tm: peak height of 18α (H), 22, 29, 30-trisnorneohopane/18α (H), 22, 29, 30-trisnorneohopane (+) 17α (H), 22, 29, 30-trisnorhopane (from m/z 191 mass chromatogram);
$C_{31}\alpha\beta$ 22S /$C_{31}\alpha\beta$ (22S+22R) hopane: 17α (H), 21β (H)-homohopane 22S/22S+22R (from m/z 191 mass chromatogram);

$C_{29}\alpha\alpha\alpha$ S/ $C_{29}\alpha\alpha\alpha$ (S +R): 5α (H), 14α (H), 17α (H)-stigmastane 20S/ 20S+20R (from m/z 217 mass chromatogram);
%C_{27}, %C_{28}, %C_{29} steranes: peak height of the R epimer of the sterane carbon number as a percentage of the sum of C_{27}R- C_{29}R steranes from m/z 217 mass chromatogram;
%C_{30} : peak height of the R epimer of the C_{30} sterane carbon number as a percentage of the sum of C_{27}R- C_{30}R steranes from m/z 217 mass chromatogram; n.m. refers to samples that are not measurable for a particular parameter because of weak signal of a particular peak.

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